

# Formation of a columnar liquid crystal in a simple one-component system of particles

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(Dated: 20 March 2015)

We report a molecular dynamics simulation demonstrating that a columnar liquid crystal, commonly formed by disc-shaped molecules, can be formed by identical particles interacting via a spherically symmetric potential. Upon isochoric cooling from a low-density isotropic liquid state the simulated system performed a weak first order phase transition which produced a liquid crystal phase composed of parallel particle columns arranged in a hexagonal pattern in the plane perpendicular to the column axis. The particles within columns formed a liquid structure and demonstrated a significant intracolumn diffusion. Further cooling resulted in another first-order transition whereby the column structure became periodically ordered in three dimensions transforming the liquid-crystal phase into a crystal. This result is the first observation of a liquid crystal formation in a simple one-component system of particles. Its conceptual significance is in that it demonstrated that liquid crystals that have so far only been produced in systems of anisometric molecules, can also be formed by mesoscopic soft-matter and colloidal systems of spherical particles with appropriately tuned interatomic potential.

## I. INTRODUCTION

Liquid crystals<sup>1,2</sup> are anisotropic phases which combine fluidity with periodicity in less than three dimensions. One-dimensional periodic order in the smectic phases arises from uniaxial stacking of liquid layers. Its spatial extent, however, is limited due to Landau-Peierls instability<sup>3</sup>, whereas the two-dimensional periodic order characteristic of columnar liquid crystals<sup>2,4</sup> is stable at the global scale. The experimentally observed columnar liquid crystals represent close packing of parallel columns composed of axially stacked molecular units. In the plane perpendicular to the column axis, the column packing forms a regular pattern with two-dimensional periodicity, whereas the remaining continuous translational symmetry dimension is directed along the column axis. The columns are commonly formed by disk-like molecules<sup>4</sup> or wedge-shaped dendrons<sup>5</sup>. The close packing of columns fixes the position of a molecule in the plane perpendicular to the column axis, but the molecules' stacking along the axis is irregular, and the axial position of a molecule is not defined with respect to its neighbors in adjacent columns, which gives rise to the continuous translational symmetry in the axial dimension.

Particle simulations have proved to be an indispensable tool for understanding the relationship between the phase behaviour and the molecular-level properties of liquid crystals<sup>6-8</sup>. These simulations have so far followed the phenomenological paradigm that dominated the science of liquid crystals for decades, whereby the structural

anisotropy of liquid crystals was assumed to be determined by anisometric shape of a molecule. Respectively, the shapes of the constituent particles in the models of liquid crystals have been designed to imitate the shapes of the molecules in the respective mesogens: the smectic phases have been simulated using rod-like particles<sup>9-12</sup>, and models of columnar liquid crystals<sup>8,13-16</sup> commonly used flat discotic particles or oblate ellipsoids.

That approach is based on the conjecture according to which formation of the structurally anisotropic liquid crystals is driven by the entropic component of the free energy<sup>17</sup>. The origin of this line of thinking can be traced to the seminal work of Onsager<sup>18</sup> which linked the anisotropy of the equilibrium structure in a liquid of rods to the entropy of packing. The conjecture of the entropic mechanism of liquid-crystal formation have been further strengthened by simulations using hard anisometric particles<sup>10,16</sup> stressing the role of the geometry of excluded volume.

A question of general conceptual interest for the statistical mechanics of condensed matter is whether the anisometry of the mesogenic molecules is really a prerequisite for producing structural anisotropy in liquid phases, as it is conjectured by the entropic paradigm, or the entropic effects on the structure formation due to the particle geometry can be compensated by an appropriately designed spherically symmetric interaction potential. This question is confined to the positional structural ordering; the nematic orientational ordering in liquids of anisometric particles is obviously beyond the scope of present discussion.

This question has been addressed in a molecular-dynamics simulation that we report here. It is demon-

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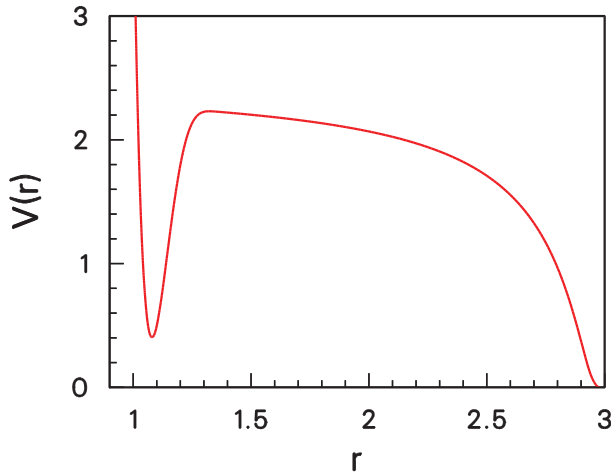


FIG. 1. Pair potential

strated that a single-component system of particles interacting via a spherically-symmetric potential can form a thermodynamically equilibrium hexagonal columnar liquid crystal. This mesophase was formed as a result of a first-order phase transition which was observed when the system had been cooled isochorically at low density from its equilibrium isotropic liquid state. A distinctive feature of this columnar phase is the liquid structure of its columns and considerable particle diffusion along the axis. Under further cooling, another phase transition took place, transforming the columnar liquid crystal into a columnar structure with global three-dimensional periodicity. This result is the first compelling evidence that an anisotropic liquid crystal phase can be produced in a system of identical particles interacting via a spherically symmetric potential. This finding opens a possibility of producing similar columnar liquid-crystal phases in colloidal and soft-matter systems composed of spherically-shape particles.

## II. MODEL AND SIMULATION

We report here a molecular-dynamics simulation of a simple single-component system of particles interacting via the pair potential shown in Fig. 1. The functional form of the potential energy for two particles separated by the distance  $r$  is defined as:

$$V(r) = a_1(r^{-m} - d)H(r, b_1, c_1) + a_2H(r, b_2, c_2), \quad (1)$$

where

$$H(r, b, c) = \begin{cases} \exp\left(\frac{b}{r-c}\right) & r < c, \\ 0 & r \geq c. \end{cases} \quad (2)$$

The values of the parameters are presented in Table I. The first term of this functional form describes the

m	$a_1$	$b_1$	$c_1$	$a_2$	$b_2$	$c_2$	$d$
12	265.85	1.5	1.45	2.5	0.19	3.0	0.8

TABLE I. Values of the parameters for the pair potential.

short-range repulsion part of the potential, and its first minimum, whereas the second term is responsible for the long-range repulsion. All the quantities we report here are expressed in the reduced units used in the definition of the potential. We also note that the short-range repulsion part of the potential, and the position of its first minimum closely approximate those in the Lennard-Jones (LJ) potential<sup>19</sup>, which makes it possible to directly compare the reduced number densities, and other thermodynamic parameters of the two systems.

It has to be mentioned that this pair potential represents a modification of an earlier reported potential<sup>20</sup> which was found to produce the smectic- $B$  crystal. The main difference between the two potentials is that in the present one the long-range repulsive part extends to a significantly larger distance. By increasing the long-range separation of the interacting particles, this modification of the potential was intended to reduce the density of particle packing in low-temperature phases where that part or interaction energy becomes significant.

The described pair potential was exploited in a molecular dynamics model comprised of 16384 identical particles confined to a cubic box with periodic boundary condition. In this simulation, we explored the phase transformations of the described system by changing its temperature isochorically at the reduced number density  $\rho = 0.3$ . Note that this density is very low as compared with the density of the LJ liquid at its triple-point,  $\rho = 0.84$ <sup>19</sup>. The temperature was changed in a stepwise manner; each temperature step was followed by a comprehensive equilibration run that typically amounted to  $10^7 - 10^8$  simulation timesteps. The temperature adjustments were performed by appropriately scaling the particle velocities.

## III. RESULTS

We began the simulation by equilibrating the system in its stable isotropic liquid state at sufficiently high temperature at the number density  $\rho = 0.3$ , which was followed by an isochoric cooling performed according to the described step-wise procedure. A discontinuous reduction of energy characteristic of the first-order phase transition was detected when the system was cooled below  $T = 1.1$ , Fig. 2. This thermodynamic singularity was accompanied by a sharp reduction of the diffusion rate. The first-order nature of the observed transition was further confirmed by a significant hysteresis which was detected when reheating the low-temperature phase, Fig. 2. An interesting peculiarity of this phase transition is that no discernable singularity in the pressure variation have been found within that range of temperature.

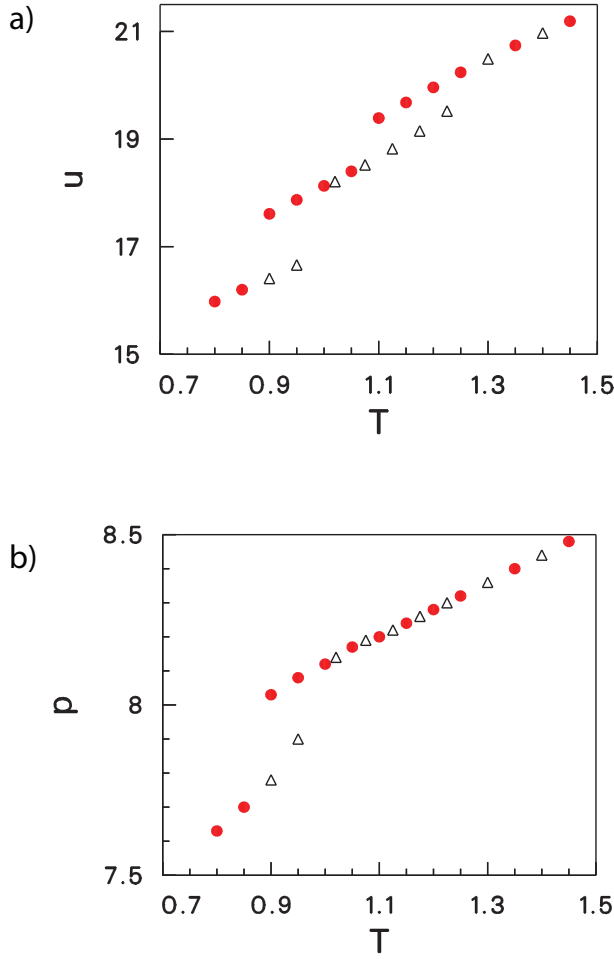


FIG. 2. Isochoric liquid-solid phase transformation. *a)* and *b)*, respectively, depict energy and pressure variation as a function of temperature. Dots and open triangles correspond to cooling and heating, respectively.

This possibly indicates a weak nature of this first-order transition<sup>21</sup>. The possibility of this kind of phase behaviour has been theoretically conjectured for columnar liquid crystals<sup>22</sup>.

We have also explored that phase transformation at constant pressure  $P = 8.16$  at the transition temperature  $T = 1.05$ , see Fig. 3. The pressure was fixed using the technique suggested by Berendsen et al<sup>24</sup>. The extremely small value of the density step upon the transition, about 0.1%, is consistent with the isochoric results in Fig. 2.

Further cooling of this phase resulted in another first-order phase transition; in this case, a clear hysteresis in both energy and pressure was observed, see Fig. 2. This transition further reduced the diffusion rate to the value characteristic of a solid phase. Thus produced low-temperature phases will hereinafter be referred to as Phase I and Phase II, according to the order of their occurrence upon cooling. Evidently, the Phase I remains in a thermodynamically stable equilibrium within a finite range of temperature.

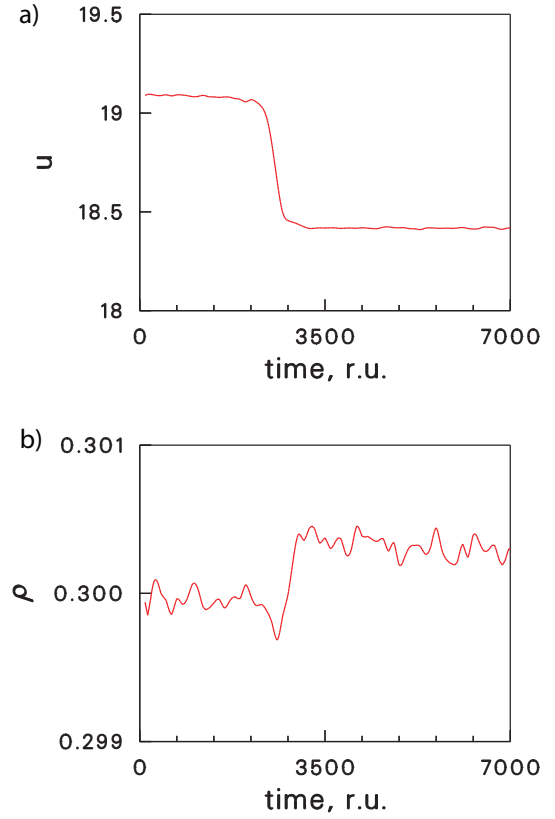


FIG. 3. Transformation of the isotropic liquid into columnar liquid crystal at constant pressure  $P = 8.16$  and temperature  $T = 1.05$ . *a)* and *b)* plots, respectively, depict variations of energy and density

The structure characterisation of the two phases has first been performed by analysing the pattern of their density correlations in the Fourier-space. For that purpose, we calculated the structure factor  $S(\mathbf{Q}) = \langle \rho(\mathbf{Q})\rho(-\mathbf{Q}) \rangle$ , where  $\rho(\mathbf{Q})$  is a Fourier-component of the number density of a system of  $N$  particles:

$$\rho(\mathbf{Q}) = \frac{1}{\sqrt{N}} \sum_{j=1}^N \exp(-i\mathbf{Q}\mathbf{r}_j), \quad (3)$$

$\mathbf{r}_i$  being the positions of the system's particles, and  $\langle \rangle$  denote ensemble averaging.  $S(\mathbf{Q})$  represents the diffraction intensity as measured in diffraction experiments.

The structure factor was first calculated on the  $\mathbf{Q}$ -space sphere of the radius corresponding to position of the first peak of the spherically averaged  $S(\mathbf{Q})$ . A well-defined pattern of  $S(\mathbf{Q})$  maxima was observed, which made it possible to determine the global symmetry and the axis. The axis orientation having been found,  $S(\mathbf{Q})$  was calculated, for each phase, in two characteristic  $Q$ -planes:  $Q_z = 0$ ,  $Q_z$  being the axis coordinate, and  $Q_y = 0$ ,  $Q_y$  coordinate corresponding to a translational symmetry vector orthogonal to the axis. The results, for both phases, are shown in Fig. 4.

These diffraction results lead us to making the fol-

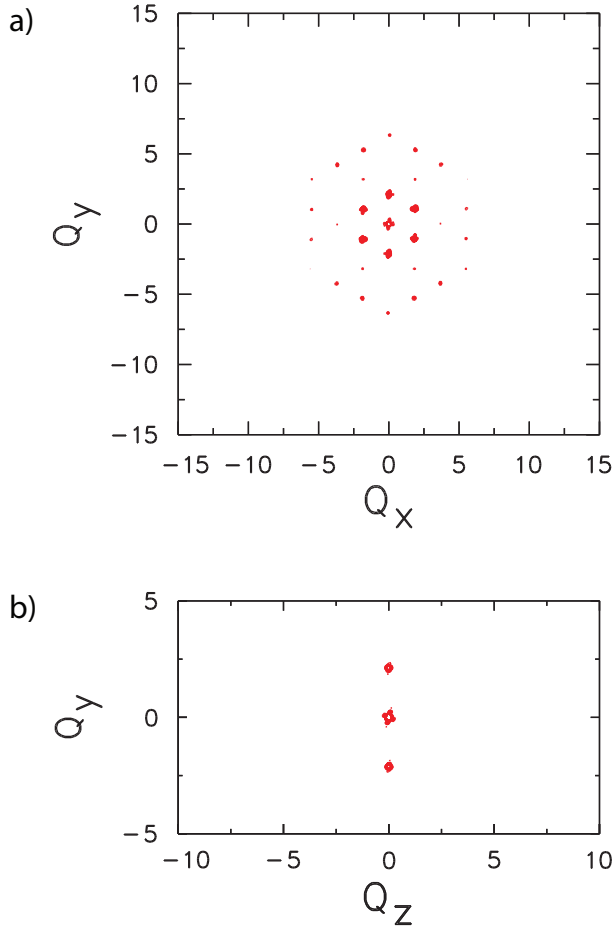


FIG. 4. The isointensity plots of the structure factor  $S(\mathbf{Q})$  calculated for a Phase I configuration in two orthogonal reciprocal-space planes. From top to bottom, respectively:  $Q_z = 0$  and  $Q_y = 0$ .  $Q_z$  denotes the axial dimension, and  $Q_y$  corresponds to one of the translational symmetry vectors orthogonal to the axis.

lowing conclusions. First, the Phase I exhibits two-dimensional global hexagonal periodicity in the plane perpendicular to the axis, whereas no structure has been found in the axial dimension. Thus, Phase I appear to be a columnar liquid crystal where parallel columns form a hexagonal close-packed pattern in the plane perpendicular to the column axis. In the axial dimension, the phase remain structureless. The transformation of Phase I into Phase II upon further cooling breaks the continuous translational symmetry in the axial dimension. Moreover, the crystalline order within column structure is induced in all three dimensions. This ordering within columns apparently occurs in a globally coherent manner, producing both axial periodicity and a periodic pattern in the plane perpendicular to the axis. The latter too is arising due to the coherence of regular packing of particles within column in Phase II. This global order is indicated by additional sets of diffraction peaks which appear in both  $\mathbf{Q}$ -planes. Thus, Phase II appear to be a

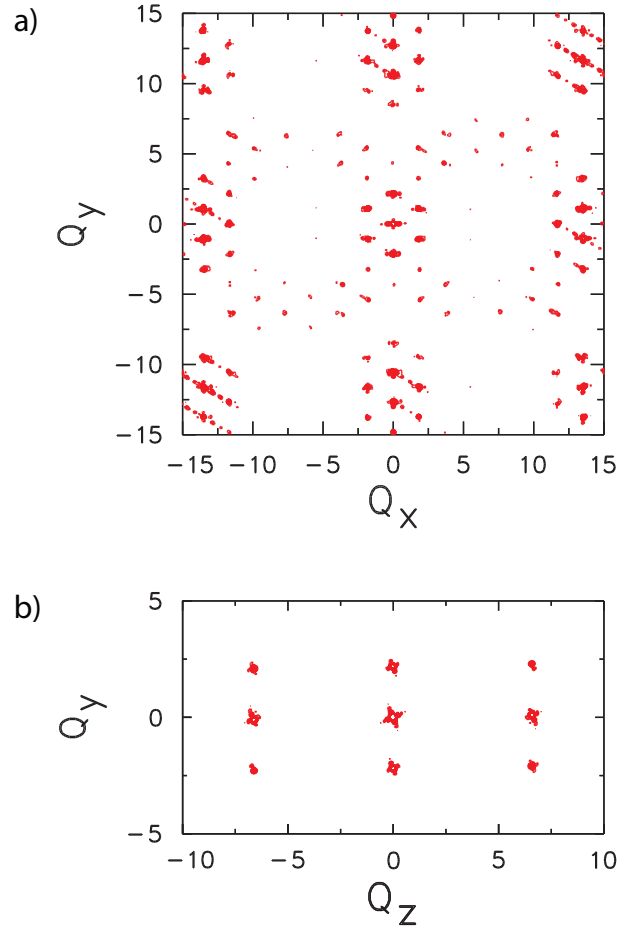


FIG. 5. The isointensity plots of the structure factor  $S(\mathbf{Q})$  calculated for a Phase II configuration in two orthogonal reciprocal-space planes. a) and b), respectively:  $Q_z = 0$  and  $Q_y = 0$ .  $Q_z$  denotes the axial dimension, and  $Q_y$  corresponds to one of the translational symmetry vectors orthogonal to the axis.

true crystal, composed of coherently arranged crystalline columns organised in the same hexagonal pattern as in Phase I. We also note that in both phases the intercolumn separation as inferred from the diffraction pattern is consistent with the long-range repulsion range of the pair potential, Fig. 1.

The conclusions about the structure of the two phases inferred from the diffraction data are consistent with the real-space images of the configurations of these phases which are shown in Fig. 6. Both Phase I and Phase II appear to be columnar structures where parallel particle columns are arranged in triangular-hexagonal pattern in the plane perpendicular to the column axis.

The most remarkable structural aspect of the Phase I that can be observed in its images in Fig. 6 is that the configuration of a column can be described as three-dimensional liquid-like dense random particle packing. This column structure is distinctively different from that ubiquitously occurring in discotic liquid crystals where the columns are composed of axially stacked disc-like par-

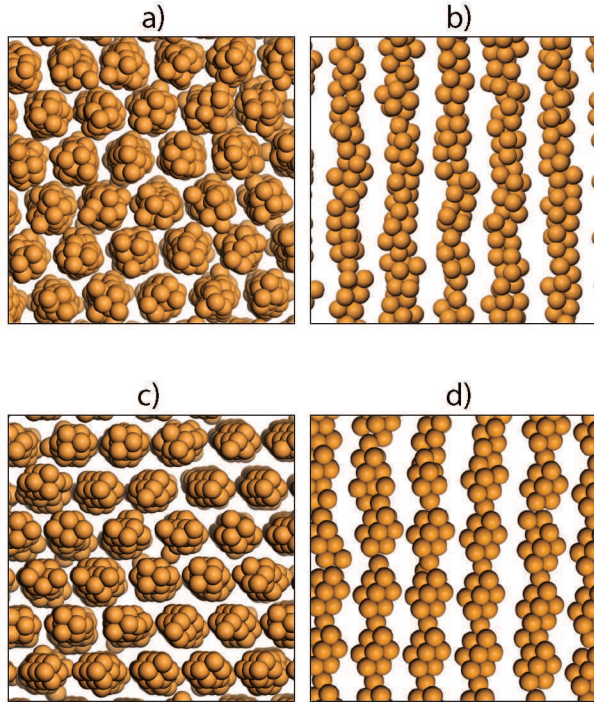


FIG. 6. The real-space images of the two phases configurations. a) and c): view from the axial direction, Phase I and Phase II, respectively. b) and d): a one-column layer of the structure, cut parallel to the layer axis, as viewed perpendicular to the axis. The particle diameter in the plot is assumed to be 1, in reduced units, which corresponds to the particles separation distance at the hard-core contact, see the pair potential in Fig.1

ticles. The discotic columns are of one-particle width, and they are densely packed laterally, forming a periodic pattern in the plane perpendicular to the axis. Under these constraints, the position of a constituent particle in a discotic phase is limited both axially and laterally. Such a structure can only allow solid-like vibrational particle motions, and the continuous global translational symmetry of the discotic phases in the axial dimension arises as a result of the lack of coherence between columns in the stacking order. By contrast, the configuration of the Phase I shown in Fig. 6 exhibits a significant spacing between its columns, and each column appears to be sufficiently wide to accommodate three-dimensional liquid-like dense random particle packing.

The characteristically liquid structure of the columns of Phase I suggests that this phase should also be expected to sustain a kind of liquid-like dynamics. Indeed, a considerable rate of intracolumn liquid-like structural relaxation has been observed (these dynamics can be seen in the movies included as supplementary material<sup>23</sup>). It is well known that atomic diffusion in dense fluids is driven by collective local particle rearrangements and, in this way coupled to the structural relaxation dynamics<sup>25,26</sup>. Driven by this diffusion mechanism, a particle is expected to be able to diffuse to unlimited dis-

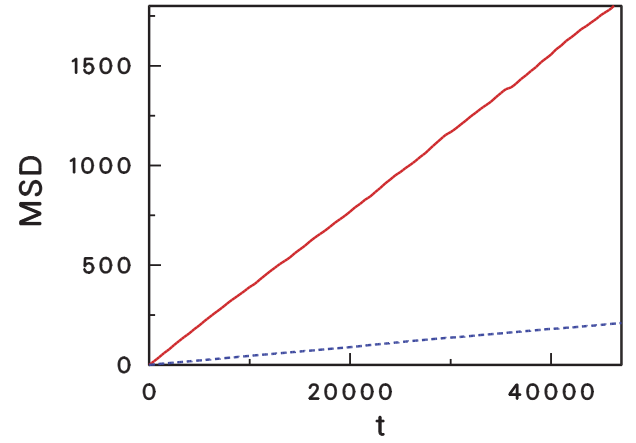


FIG. 7. Mean-square particle displacement (MSD) in Phase I as a function of time at  $T = 1$ . Solid line corresponds to the diffusion along the column axis. Dashed line: MSD averaged over directions perpendicular to the axis

tance within a column along the axis, whereas its transition perpendicular to the axis is limited by the column diameter. A particle can, nevertheless, leave the column by hopping to an adjacent one; these hopping events, however, are expected to be rare relative to the particle intra-column diffusive movements because of the large energy cost of crossing the potential-energy maximum separating the columns, see Fig.1 (the occasional intercolumn particle hoppings can be observed in the movie included as supplementary material). Driven by these two distinctly different diffusion mechanisms, the particle diffusion in Phase I is therefore expected to be strongly anisotropic, with its gradient directed along the axis. This conjecture is confirmed by the mean-square particle displacement data presented in Fig. 7 which demonstrate that particles indeed diffuse in the axial dimension much faster than in a direction perpendicular to the axis. These results convincingly demonstrate that a constituent column in the Phase I represents a genuine three-dimensional liquid, both structurally and dynamically.

One can also see in Fig. 6 that the transition of the liquid crystal (Phase I) into a crystalline phase possessing a three-dimensional periodicity (Phase II) represents a structural transformation of the liquid configuration of each column into a three-dimensional periodic crystal configuration. It is also possible to see that the axial periodic order of a crystalline column is coherent with that of the neighbour columns, thereby producing a global axial periodicity. In the reciprocal space pattern, this gives rise to the respective diffraction peaks emerging in the axial reciprocal-space plane, see Fig. 5. Moreover, the periodic order arising within a column in the process of its crystallisation in the directions perpendicular to the axis develops in a manner coherent with the respective order in the neighbour columns. Thereby a pattern of global periodicity with wave vectors defined by the close-

neighbour distance arises perpendicular to the axis, giving rise to a set of additional diffraction peaks which appears in the respective reciprocal-space plane as a result of the Phase II formation, see Fig. 5. We note that the planes of periodically stacked particle layers in Phase II that can be observed from the view perpendicular to the columns, Fig 6. A detailed analysis of this crystal structure will be reported elsewhere.

#### IV. DISCUSSION

Following the seminal work of Onsager<sup>18</sup>, the science of liquid crystals has been dominated by the entropic paradigm according to which anisometric shape of the constituent particles is a prerequisite for the formation of anisotropic structure in liquids<sup>17</sup>. A conceptually significant implication of the present result is that it directly contradicts that long-standing opinion. We have demonstrated that an anisotropic pattern with two-dimensional global periodicity can emerge in a liquid composed of a single sort of particles interacting via a spherically-symmetric potential. Moreover, this liquid phase has also demonstrated a strongly anisotropic self-diffusion. This result thus makes it possible to conclude that emergence of structural and dynamic anisotropy in a liquid phase is not necessarily related to the entropic component in the free energy that has so far been assumed to be responsible for the formation of equilibrium anisotropic liquid phases.

Moreover, the Phase I represents a novel type of columnar liquid crystal distinctively different from those commonly observed in discotic systems. In the discotic columnar phases the time-averaged positions of constituent particles are fixed due to the structural constraints imposed by the intracolumn stacking order and the close-packing of the columns. In contrast, the liquid crystal that we discovered in this study is a genuine liquid phase, both structurally and dynamically. Its columns demonstrate a three-dimensional liquid-like structure and a high rate of structural relaxation dynamics (see the movie in supplementary material) which mediates a predominantly axial diffusion, see Fig 7. The possibility of a liquid phase with uniaxial self-diffusion may be of a significant technological interest.

Another interesting aspect of the liquid-crystal formation we report here is its apparent similarity to the microphase separation transition<sup>27</sup>. The latter is commonly observed in some polymer blends which, instead of macroscopic phase separation, are able to form under cooling an equilibrium structure of microscopic-size domains with different polymer concentration. These microdomains may form different kinds of globally ordered superstructures, including hexagonal symmetry similar to the one we observed in this simulation. Both the structures produced by microphase separation and the present columnar phase exhibit an anomalously low amplitude of density modulation characteristic of weak crystallisation

transition<sup>21</sup>. The simulation we report here thus demonstrates that the microphase separation can be produced in a simple system of identical particles using a potential with short-range attraction and long-range repulsion.

One possible way of realisation of this model in terms of physical systems is straightforward. Columnar liquid crystals have so far been produced in colloidal systems of anisometric particles, commonly of disk-like shape. The present result suggests that columnar liquid crystals with the structure similar to that we report here, and possibly other liquid-crystal phases, can be formed by spherical colloidal particles, with appropriate tuning of the effective force field. It has to be mentioned that the main features of the pair potential we exploited in this simulation are consistent with the classical theory for colloidal interactions by Deryagin, Landau, Verwey and Overbeek (DLVO)<sup>28–31</sup>, amended with hard-core repulsion or steric repulsion close to the contact. We also mention that a family of similarly-shaped pair potentials have been used to produce patterns in two-dimensional simulations of soft-matter systems<sup>32</sup>

#### V. CONCLUSION

In summary, we have presented a molecular dynamics simulation which demonstrates that a thermodynamically equilibrium hexagonal columnar liquid crystal can be formed in a simple single-component system of particles as a result of a first-order phase transition from an isotropic liquid phase. This result is the first demonstration that liquid crystals that have so far only been found in mesogenes composed of anisometric molecules can also be formed in a system of identical particles with spherically-symmetric interparticle pair potential. Another conceptually significant distinction of this liquid crystal as compared with commonly observed discotic phases is that its columns are structurally and dynamically fluid; we observed a considerable diffusion along the column axis. The scope of impact of this finding is expected to include a possibility of producing columnar liquid crystals in colloidal systems of identical spherical particles and other similar soft-matter mesoscopic particle systems.

#### VI. ACKNOWLEDGEMENTS

We thank Dr. B. Sadigh for very useful discussions. This study was supported by the Swedish E-Science Research Foundation (SERC). Funding from the Swedish National Research Council (VR) is gratefully acknowledged. This work has been approved for release under Lawrence Livermore Release No. LLNL-JRNL-656140.

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